15th International Drying Symposium (IDS 2006)
Budapest, Hungary, 20-23 August 2006

NEW INSTRUMENT FOR MEASUREMENT OF KILN EMISSIONS IN DRYING OF SOFTWOOD TIMBER AND RESULT ANALYSIS

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Abstract: In timber drying, VOC emissions have negative impacts on human health and environment and, therefore, should be controlled under certain level. In this work, a new instrument called SIFT-MS (Selected Ion Flow Tube--Mass Spectrometer) was tested and used for detection of the timber drying emissions. The results showed that the SIFT-MS is an accurate technique and its portable version, which is being developed, will be a useful measurement device. By using this instrument, compounds and levels of the emissions were measured at different drying stages for five drying schedules with drying temperature from 70 to 120°C.

Keywords: timber drying, kiln emissions, volatile organic compounds (VOCs,) Selected Ion Flow Tube – Mass Spectrometer (SIF-MS)

INTRODUCTION

During the drying of softwood timber a complex range of chemical compounds are either volatilised, steam distilled, or derived from the thermal degradation of cell wall components of the wood. These emissions will typically consist of monoterpenes, methanol, acetic acid and formaldehyde. Environmental concerns relating to discharges of volatile organic compounds (VOC) arise since they are potential precursors for photochemical formation of ozone, other atmospheric oxidants and aerosols.

Among the chemicals emitted, formaldehyde, methanol and acetaldehyde are the most concerned emissions which have negative effects on health and the environment (Website 1). Acetaldehyde irritates the eyes, skin and respiratory tract, paralysis and death may occur at high concentrations. Formaldehyde irritates the eyes, nose and throat and causes respiratory and reproductive problems. Methanol causes visual disturbances, blindness, headaches, giddiness and insomnia. Due to the negative effects on health of these substances, they need to be dealt with seriously when present in any reasonable quantities.

Table 1 – Effects of wood emissions on human health

Compound	Exposure Limit (ppb*)	Effect of Exposure
Formaldehyde	300	Irritates eyes and respiratory tract.
Acetaldehyde	10,000	Irritates eyes and respiratory tract.
Formic Acid	5,000	Corrosive to eyes, skin and respiratory tract.
Acetic Acid	10,000	Corrosive to eyes, skin and respiratory tract.

ppb: parts per billion.

Unfortunately, there are no international regulations in place to limit the emission level in the industry, partly due to the resistance from industry and partly due to the lack of reliable instrument to accurately detect the emissions.

Current work has been conducted to achieve two objectives. The first one is to find and test suitable detection instrument which can give high accuracy

for the emission detection and is accepted by industry. The second objective was to quantify the emitted components in the VOCs from drying of softwood timber thus the current emission can be quantified.

In this work, lab scale drying tests were performed for the emission detection. Lavery and Milota (2000) have found that the commercial kiln emitted an average of 0.87g of VOCs per kg of oven dry wood and the laboratory kiln averaged 0.79g per kg oven dry wood. Therefore, the results from a laboratory kiln can represent a commercial kiln reasonably well.

EQUIPMENT

Drying Tunnel for Wood Drying

The drying tunnel in the Department of Chemical and Process Engineering at the University of Canterbury was utilised for the drying experiments. Shown in the back of this paper, Fig. 1 is a schematic diagram of the tunnel which has a computer for control and data acquisition by connecting to sensors installed inside the tunnel and to valves for steam injection.

Details of each section in the tunnel have been described by McCurdy (2000), and briefed as follows. The Settling Chamber has a large cross sectional area which slows the air velocity through this section. The reduction in air speed is necessary to limit pressure drop across the meshes. The mesh screens are in place across the exit of the settling chamber to minimise air turbulence. Next, the air flows through the contraction cone, it has two purposes. Firstly, this cone section is to reduce the tunnel size down to that of the test section thus increasing airspeed and, secondly, it is curved to provide a uniform flow profile at its exit. The samples are tested in the test section which has an even square cross section along its length and a door for access to the sample holder. The sensor section is in the downstream of the sample zone with the temperature and humidity sensors being installed.

The tunnel is controlled by a PC running Advantech® Genie™ data acquisition and control software. This package controls temperature and humidity of the air as well as the air velocity. It records data from the mass balance, temperature and humidity sensors.

The SIFT-MS for Emission Measurement

The SIFT-MS (Selected Ion Flow Tube Mass Spectrometer) has been researched and developed over the past 20 years by the Chemists in the Department of Chemistry at the University of Canterbury. It is a useful device for detecting and quantifying trace gases down to the ppb level. Previous applications include detection of gas compounds in explosions and human breathing for disease diagnosis. With the success of such applications, a company, Syft, was formed who provides services and supply equipment. With recent modification, the instrument becomes portable thus is suitable for application in wood drying industry for detection of kiln emissions. The apparatus is fairly complex although recent developments have reduced its size which its schematic diagram shown in Fig. 2 in the back of this paper, in which main sections of the apparatus are labelled.

The precursor ions are created in an ion source external to the flow tube. For this project H_3O^+ are the ions used. These are created from water in a flow of argon carrier gas. They are then extracted from their source using the quadruple mass filter which selects them according to mass to charge ratio. The extracted ions are injected into the helium carrier gas. The carrier gas and the single ion species are carried by convection along the flow tube.

To measure concentrations of compounds in a sample of gas, the gas is introduced at a known flow into the carrier gas. The downstream mass spectrometer measures the count rates of both the precursor ion and the products it makes with the VOCs in the sample. By relating count rates to number density of the reactant gas and the rate of reaction the ion products can be determined.

To quantify the concentration of analyte present in a sample of gas a number of variables must be known. Information about the type of precursor ion, the rate of reaction between the analyte and ion and the products formed from this reaction must all be specified. These variables form the basis for the kinetic file used in the SIFT-MS software that analyses gas samples for specific compounds. The concentration of the analyte in the flow tube is given by the following equation:

$$[A] = \frac{1}{t} \frac{\sum_{1}^{n'} I_{Si} d_{Si}}{\sum_{1}^{n} k_i I_{Pi} d_{Pi}} \qquad (1)$$

The value of t can be obtained by using Eq. (2):

$$t = \frac{v_i}{l} \qquad (2)$$

Where v_i is the ion velocity which is equal to $1.5v_g$ and the value of v_g is determined from:

$$v_g = \frac{4 F_g T_g}{273 \pi P_{ft} d_{ft}^2} \qquad (3)$$

Using the Eqs. (1) to (3), the SIFT-MS instrument with its associated programmes is able to quantify the concentrations of gases in the feed sample in parts per billion (ppb).

EXPERIMENT

Drying Tests

Five different drying schedules as given in Table 2 were used with an intention to investigate the effects of drying temperature and humidity (wet-bulb temperature). Matched rough sawn timber of *Pinus radiata* sapwood was used in the experiment, three pieces in the high temperature (120/70C) run and one piece for each of other drying runs. Each piece was approximately 100mm wide, 50mm thick and 800mm long. Before the start of each run, the steam injection and electric heating system were turned on for the conditions to reach the set points.

Table 2: Drying schedules used for the experiments

Run	Dry-bulb (°C)	Wet-bulb (°C)	Final MC (%)
1	70	60	12
2	90	50	6
3	90	60	13
4	90	70	6
5	120	70	14.3

After the tunnel conditions reached the set points, the sample board(s) were weighed and placed inside the test section of the tunnel with approximately 20mm space to allow air to flow across all surfaces. The door was closed as soon as possible to reduce the loss of heat from the kiln and the samples were dried to a final moisture content of 6-14%.

Gas Sampling and Testing

Gas samples were collected at intervals of four to eleven times throughout each drying cycle, depending on the total drying time of the schedule. The samples were taken from a port on the top of the tunnel at the rare position of the test section. A diffusion membrane air pump was used to draw gas out of the tunnel and to fill a Mylar balloon. The balloons used had a filling valve ensuring no loss of sample or contamination from the outside air during the sample collection process.

The gas samples were taken for testing in the SIFT-MS at the Syft laboratory in Christchurch, New Zealand. Each sample was analysed within 12 hours of collection to minimise any possible reaction of sample analyses with the balloon substrate. The inlet tube of the SIFT-MS was inserted into the balloon and the vacuum conditions within the device cause the sample gas to be introduced to the flow tube at a steady rate. Data on the VOCs of interest and the products formed with the precursor ions had been entered into a programme code. This allowed immediate identification and quantification of the VOC compounds.

The VOC concentration was analysed together with the samples dried to calculate the total quantity of VOCs emitted during each drying schedule and the emission rate. The moisture lost from the wood samples throughout an entire drying run was determined from initial and final mass of the samples. The absolute humidity difference between the air inside the tunnel and the ambient air was determined based on the drying conditions and ambient air conditions. This made it possible to calculate the total mass of air required to flow through the tunnel during the period of drying. In this way, the total mass of VOC emissions was quantified.

RESULTS AND DISCUSSION

The emission compounds and average concentrations for each run of the drying tests are given in Table 3. From the results, it was found that eight major compounds have been detected at the ppb level by using the SIFT-MS instrument. It is confirmed that this instrument can give very accurate detection although it is compact in size. The most remarkable advantage over other techniques is that the SIFT-MS can measured all of the eight compounds at once which is impossible for other techniques. The eight compounds include acetic acid, acetone, formaldehyde, acetaldehyde, methanol, ethanol, pinenes and formic acid. The concentrations of these compounds vary with drying schedules but, for most of the schedules, pinenes is the most prevalent emission. However, the most concerned compound is formaldehyde which concentration was at around the limit to adversely affect human health.

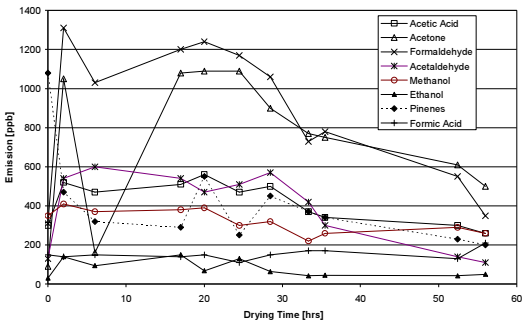

Fig. 3. Emissions for drying schedule of 70/60°C

Fig. 3 shows that concentration changes with the drying time for schedule of 70/60°C. The bulk of emission came from formaldehyde and acetone followed by acetaldehyde and acetic acid. With particularly concern is formaldehyde emission which is well above the limit level to cause human's eye and respiratory irritation. Fig. 3 also showed that there were two major peaks of volatile organic emissions, the first peak was about two hours after drying and the second peak was between 20-30 hours after drying. The first peak may correspond to the

surface temperature initially rising to the wet-bulb temperature. The second peak in emissions occurred in the middle of the drying process when the wood was dried to the fibre saturation point (about 26% MC). Around this time, internal diffusion, not surface evaporation, controlled the drying rate and the wood temperature increased. Further studies are being conducted to confirm whether this high level of formaldehyde emission is due to the schedule or due to the wood variability.

For the three 90°C schedules, the objective was to investigate the effect of humidity with different controlled wet-bulb temperatures. The total emission concentrations as a function of drying time are shown in Fig. 4. In general, the emission concentration decreased with the drying time and the emissions at the high humidity schedule (90/70°C) were the highest whereas the other two schedules did not show significant differences. The most prevalent compound for the three schedules was pinenes but the values for other major compounds were different.

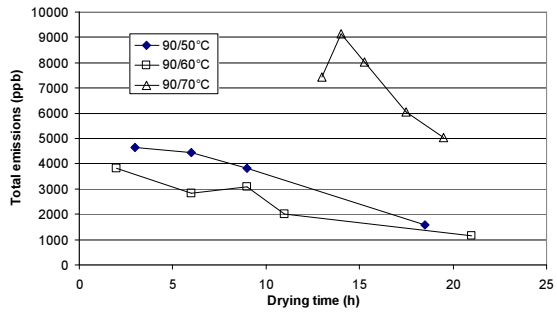

Fig. 4. Total emissions with drying time for 90°C schedules

In the drying at 90/50°C, following pinenes (1032.5ppb) was methanol (687.5ppb), acetaldehyde (645ppb) and formaldehyde (462.5ppb). The emission trend as a function of drying time showed that the highest emission was after nine hours of drying and then tended to level out or drop dramatically. In the run of 90/60°C schedule, apart from pinenes (1184ppb), methanol (526ppb) contributed to the emission most and the bulk of the volatile organic compounds was emitted after nine hours of drying. For drying at 90/70°C, the acetic acid (4800ppb) dominated the VOC emissions followed by pinenes (749.2ppb), formaldehyde (394ppb) and methanol (470ppb). The bulk of the volatile organic compounds was emitted after 14 hours of drying and again at around 17.5 hours of drying.

The three 90°C schedules did not show remarkable peak except for the 90/70C one. Generally, the emissions of VOC tended to decrease toward the end of drying. This was particularly obvious in the drying schedule 90/50°C. By comparing the total emission, it was found that schedule 90/60°C emitted the lowest VOC despite having a lower relative humidity than schedule of 90/70°C. Therefore it can be concluded that relative humidity was not the major factor affecting the emissions. The final moisture content and the drying time appeared to affect VOC emission. The final moisture content was 6% and 13% for schedule 90/70°C and 90/60°C respectively, and the prolonged drying to low moisture content increased the total amount of VOC.

The results for the emissions from the high temperature 120/70°C schedule are shown in Fig. 5, displaying similar trend to the other runs with methanol (834ppb), acetaldehyde (630ppb) and acetone (416ppb) providing significant emissions after pinenes (11,744ppb). In this case, pinenes emissions were significantly higher than those in other schedules. The trend of most VOC emissions to decrease with duration of drying was again apparent, as was the familiar profile of formaldehyde with the peak emissions occurring midway through the drying process.

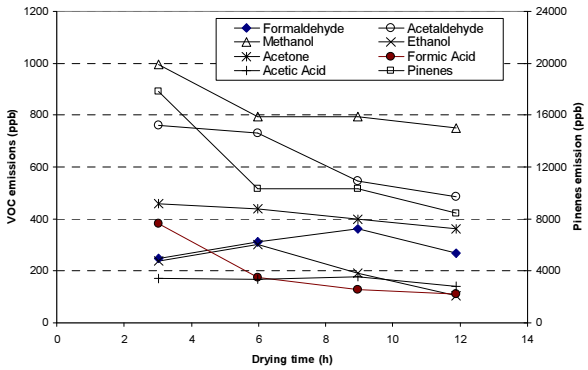

Fig. 5. Emissions for drying schedule of 120/70°C

For all of the schedules tested, the 120/70°C schedule produced the highest emission of 14,493 ppb on average, followed by the 90/70°C (7134ppb) and 70/60°C schedules. However, the most concerned compound of formaldehyde had concentrations in the above three schedules higher than the limit which adversely affects human health (Table 1). The results show that the formaldehyde concentration was high in the early stage of low temperature drying but in late stage in high temperature drying. By knowing this, the operators should take cautious procedures to enter the kiln for checking the drying. Considering that the exhausted air is dispersed once out of the vents, the concentration near the timber drying kiln is much lower during normal drying operations thus exposes much less impacts. However, future research is needed to investigate the concentration distribution around the timber drying kiln, particularly, when a number of commercial scale kilns are installed in one site.

Although methanol and ethanol is regarded as a human toxicant, their occurrence in kiln emissions is unlikely to cause adverse occupational or environmental effects. The maximum concentration of methanol emitted on average was 687.5 ppb and the highest emission was 860 ppb at drying schedule of 90/50°C. The emission of ethanol for each drying schedule was generally low, therefore, it was also unlikely to have any adverse effects, as it was most likely to be below the exposure limit.

All of the drying schedules showed the presence of pinenes, which was expected to make up the bulk of the emissions concentration. Although at high concentration, the pinenes is not expected to cause noticeable impact on human health and environment.

The emissions has also been analysed in terms of the emission rate per volume of timber (g/m^3 wood) and the emission rate per volume of timber in unit time (g/m^3/h). The figures of emission rate for each drying run are also given in Table 3. The rate of emission was greatest for drying schedule 90/50°C at 5.2 g/m^3/h, therefore even though it had a short drying time, the VOC emission was the highest. Likewise, the 70/60°C schedule had a lower rate of emission (1.5 g/m^3/h) than schedule 90/70°C and 90/60°C, but because its drying time was the longest, the absolute VOC emission was high.

The total concentration of VOC emitted at drying schedule 120/70°C was high (11744 ppb) but due to the greater volume of wood used (three pieces) the emission rate (1.6 g/m^3/h) was lower than the 90°C schedules.

CONCLUSIONS

Emissions from timber drying kiln can be accurately measured by using the newly developed instrument, Selective Ion Flow Tube – Mass Spectrometer (SIFT-MS). Eight compounds can be detected at ppb (parts per billion) level, including acetic acid, acetone, formaldehyde, acetaldehyde, methanol, ethanol, pinenes and formic acid.

For the drying schedules tested except for the low temperature drying at 70/60°C, the most prevalent compound is pinenes ranging from 749.2 to 11744 ppb. However, the most concerned compound is formaldehyde which concentration is generally higher than the limit which adversely affects human health. The indication from the study is that the kiln drying operators should take careful procedures if entering the kiln to check the wood during drying.

The drying schedules do not appear to consistently affect the emissions. The high temperature schedule gives highest emission concentration but the emission rate (g/m^3/h) is not the highest. On the other hand the 90/50C schedule generates the highest emission rate (g/m^3/h) among the schedules examined. The emission rate considers the wood volume dried and the drying time.

Some factors are considered to contribute to uncertainties in the results. The first one is the actual conditions (temperature and humidity) inside the drying tunnel which fluctuated away from the set points during drying. This may have caused major disturbance in the VOC emission. The final moisture content of the wood samples was not the same, therefore making it hard to compare the different schedules. The wood samples were not collected from the same tree and presence of any heartwood in the tests samples would probably have emitted higher concentration of VOC.

NAMENCLATURE

A:	Analyte concentration	ppb
d_{ft}:	Flow tube diameter	m
d_{Pi}:	Diffusion factor for precursor ion	-
d_{Si}:	Diffusion factor for product ion	-
F_g:	Gas flowrate	L/s
I_{Pi}:	Intensity of precursor ion	counts/s
I_{Si}:	Intensity of product ion	counts/s
k_i:	Rate of reaction of precursor and analyte	cm^3/s
l:	Length from sample inlet to orifice	m
P_{ft}:	Flow tube pressure	Torr
T_g:	Gas Temperature	K
t:	Reaction time	s
v_i:	Ion velocity	m/s

REFERENCES

Lavery, M.R. and Milota, M.R. (2000), VOC emissions from Douglas-fir: Comparing a commercial and a laboratory kiln. *Forest Products Journal,* Vol.50, No.7/8, pp.39-47.

McDonald, A.G. and Wastney, S. (1995), Analysis of volatile emissions from kiln drying of radiate pine, *Proceedings of International Symposium on Wood and Pulping Chemistry*, Helsinki, Finland, pp.431-436.

McCurdy M.C. (2000), Moisture Movement and Strain Development in *Pinus radiata* Boards during High-temperature Drying. M.E. Thesis, University of Canterbury, Christchurch, New Zealand.

Wu, J. and Milota, M.R. (1999), Effect of temperature and humidity on total hydrocarbon emissions from Douglas-fir lumber. *Forest Products Journal*, Vol.49, No.6, pp.52-60.

Website, www.ilo.org/public/english/ protection/ safework/cis/products/icsc/dtasht/index.htm

Table 3. VOC emission compounds and average concentrations (ppb) for various schedules

Compounds	Drying schedule				
	70/60	90/50	90/60	90/70	120/70
Acetic acid	510	315	78.4	4800	165
Acetone	1080	98.8	186	165.4	416
Formaldehyde	1200	462.5	99.8	394	298
Acetaldehyde	540	645	164	291	630
Methanol	380	687.5	526	470	834
Ethanol	150	172.5	72.4	117.4	209
Pinenes	290	1032.5	1184	749.2	11744
Formic acid	140	200	258	146.8	198
Total	4290	3614	2569	7134	14493
Total emissions (g/m^3 wood)	95	95.9	49.5	84	31.2
Total emissions (g/m^3 wood/h)	1.5	5.2	2.3	3.5	1.6

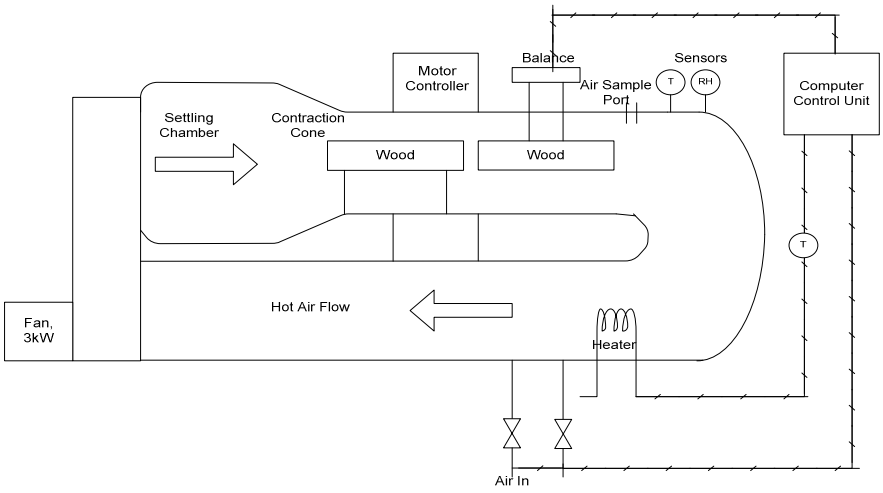

Fig.1. Denham Laboratory Drying Tunnel.

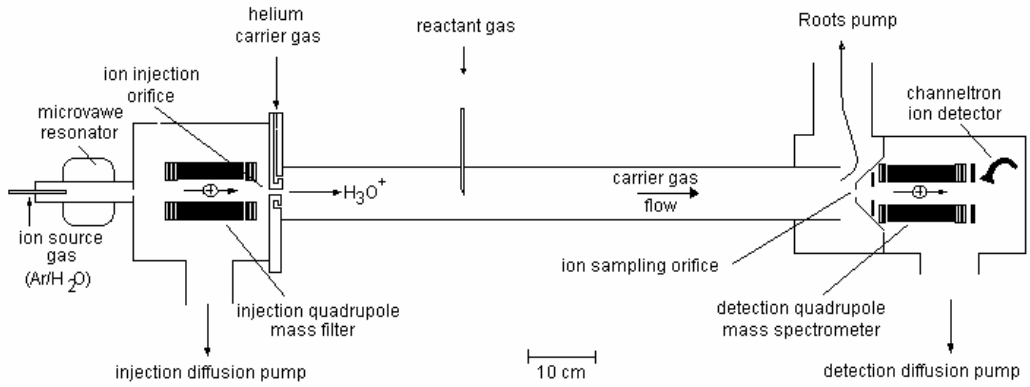

Fig.2. The SIFT-MS Instrument